ELECTRIC CONDUCTIVITY OF IODINE SOLUTIONS
III. ELECTRIC CONDUCTIVITY OF THE SYSTEM: I-Me$_4$NI.

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ABSTRACT. Electric conductivity of the system I-Me₄NI
was detd. up to 9.2 mol. % of the latter at 130, 140
and 150°. It rapidly increases with concn. and reaches
the magnitude of 0.1 mho at 5 mol. %; beyond this concn.
the rate of increase of sp. cond. is less, and at the
highest concn. used it is 0.171 mho at 130° and 0.189 mho
at 150°. Comparison of sp. and mol. conductivities of this
system and those of I solns. of KI and RbI shows considerable
similarity of isotherms of cond. and in respect to variations
with concn. and temp. The electrolyte in the system
studied is considered to consist of assocd. mols. of
probable formula $(Me_4NI_9)_2$.

Iodine solutions of alkali metal iodides and thallium iodide have considerable /753*
electroconductivity, on the order of 10^{-1} mho even with comparatively low iodide
concentrations [1, 2]. In these systems, the electrolytes can be polyiodides or
associated molecules of the iodides themselves.

Experimental data show that the electroconductivity of iodine solutions is
related to the association of iodides dissolved in melted iodine: iodides
(HgI_2, SnI_4, PI_3, SbI_3) with normal molecular weight in iodine [2] do not signifi-
cantly affect the electroconductivity of liquid iodine; iodides of alkali metals
[3], as well as AlI_3 and TlI^4, associated in iodine, with it form current conduction
systems.

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*Numbers in the margin indicate pagination in the original foreign text.

At the same time, thermal analysis of the systems: iodine-iodide of alkali metals [5]*, I_2-TlI [5], I_2 -AlI_3 [7], as well as a number of other systems composed of iodine and iodides of tin [3], arsenic, antimomy [9], bismuth [10], mercury [11], selenium and several others [12], do not form polyiodides.

Taking all these data into consideration, it has been concluded that the electroconductivity of iodides in liquid iodine is due to the electrolytic dissociation of associated iodide molecules, and not the formation of polyiodides.

The fact that many of these iodides form polyiodides easily only in aqueous and nonaqueous solutions (where these polyiodides are usually precipitated out of the solutions in the form of crystalline hydrates or solvates) can be explained as follows: molecules of the solvent, solvating a cation of haloid salt, increase their volume and thereby reduce their polarizing effect; as a result, there is a decrease in the resistance of the complex ion $[I(I_2)_n]'$, in which the coordination bond between the iodine anion and the iodine molecules is realized by unidirectional polarization by the field of the central negatively-charged iodine ion of coordinated iodine molecules**.

This can explain the well-proven formation of simple polyiodides in the absence of a solvent*** for salts whose cation has a large ion radius, for example, for iodides of tetrasubstituted ammonium bases. Thus, Olivari [11], by thermal analysis of the systems $(CH_3)_3C_6H_5NI-I_2$ and $(CH_3)_4NI-I_2$, proved the formation in these systems of several (tri, penta, hepta and ennea) polyiodides.

Geuther [13] and Stromholm [14] produced a large number of polyiodides of this /754 type by crystallization from alcohol solutions.

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*According to the data of Briggs [6], only in the $CsI-I_2$ system can the formation of a CsI_3 and CsI_4 compound be assumed. However, this conclusion is based on a very small amount of insufficiently determined experimental data.

**In other words, we can say that the increased volume of the cation weakens contrapolarization, which the complex ion experiences on the part of the cation.

***Or the formation of polyiodides which do not contain a molecule of the solvent.

Taking these facts into consideration, we felt it would be interesting to study the electroconductivity of iodine solutions of tetramethylammonium-iodide and compare it with that of iodine solutions of alkali metal iodides to determine how the formation of polyiodides in iodine solutions affects the increase of electroconductivity and the character of its isotherm.

MATERIALS, RESEARCH TECHNIQUE AND RESULTS OBTAINED

Iodine — a preparation of resublimatim purissimum — was sublimated several times with KI and BaO and once without. Sublimated iodine was dessicated over dry potassium hydroxide for 5-6 days.

The electroconductivity of the iodine obtained in this way was $1.43 \cdot 10^{-5}$ and $3.02 \cdot 10^{-5}$ mho at 140°. The lowest electroconductivity of iodine, according to the data of Lewis and Wheeler [2], is $2.10 \cdot 15^{-5}$ at 140°; according to the measurements of M. Rabinovich [15], it is $4.48 \cdot 10^{-5}$ mho at 138.2°, and according to our data [1], at 140° it is $0.75 \cdot 10^{-5} - 3.03 \cdot 10^{-5}$ mho.

Tetramethylammonium-iodide was used in the form of a Kahlbaum preparation.

Electroconductivity was measured by the Kohlrausch-Ostwald method with a various capacity generator. The electroconductivity vessel had the shape indicated in the first report. Electrodes were not plantinized. A vessel with ordinary flat electrodes was used with small iodide concentrations; for large concentrations, because of the great reduction in resistance (1 ohm or less), in order to avoid measurement errors, we were forced to reduce the area of the electrodes significantly, and for this purpose used a vessel with platinum wire electrodes.

Electroconductivity was measured at 130, 140 and 150° in a thermostat with Vaseline oil, externally heated. Temperature variations did not exceed 0.2-0.3°. Minumum sound was heard very clearly in the 0.5-1 mm interval, which is typical of bromine and iodine solutions.

First the electroconductivity of the iodine was measured; a suspension of $(CH_3)NI$ was introduced into the cooled vessel (from a suspended small glass ampule), the vessel was placed in a thermostat heated to 150°, the melt was care-

TABLE 1. ELECTROCONDUCTIVITY OF THE SYSTEM $(CH_3)_4NI - I_2$

Concentration		Specific electroconductivity			Dilution	Molecular electro-conductance at 140°
wt. %	molar %	130°	140°	150°		
0	0	$1,44 \cdot 10^{-5}$	$1,43 \cdot 10^{-5}$	$1,42 \cdot 10^{-5}$	—	—
0,05	0,06	$4,32 \cdot 10^{-4}$	$4,29 \cdot 10^{-4}$	$4,25 \cdot 10^{-4}$	102 150	4,24 *
0,10	0,13	$8,82 \cdot 10^{-4}$	$8,56 \cdot 10^{-4}$	$8,44 \cdot 10^{-4}$	51 560	43,41
0,20	0,25	$2,19 \cdot 10^{-3}$	$2,18 \cdot 10^{-3}$	$2,18 \cdot 10^{-3}$	25 860	56,12
0,30	0,38	$3,84 \cdot 10^{-3}$	$3,84 \cdot 10^{-3}$	$3,84 \cdot 10^{-3}$	18 940	72,54
0,40	0,50	$5,85 \cdot 10^{-3}$	$5,69 \cdot 10^{-3}$	$5,85 \cdot 10^{-3}$	12 970	73,67
0,50	0,62	$8,12 \cdot 10^{-3}$	$8,17 \cdot 10^{-3}$	$8,19 \cdot 10^{-3}$	10 426	85,08
0,79	1,00	$1,62 \cdot 10^{-2}$	$1,64 \cdot 10^{-2}$	$1,65 \cdot 10^{-2}$	6528	107,06
0,99	1,24	$2,22 \cdot 10^{-2}$	$2,25 \cdot 10^{-2}$	$2,28 \cdot 10^{-2}$	5249	118,10
1,48	1,86	$2,86 \cdot 10^{-2}$	$3,76 \cdot 10^{-2}$	$3,79 \cdot 10^{-2}$	3547	133,37
1,96	2,47	$5,13 \cdot 10^{-2}$	$5,30 \cdot 10^{-2}$	$5,39 \cdot 10^{-2}$	2672	141,62
2,43	3,06	$6,59 \cdot 10^{-2}$	$6,69 \cdot 10^{-2}$	$6,89 \cdot 10^{-2}$	2157	144,30
2,91	3,65	$7,89 \cdot 10^{-2}$	$8,20 \cdot 10^{-2}$	$8,46 \cdot 10^{-2}$	1815	148,83
3,38	4,24	$9,25 \cdot 10^{-2}$	$9,43 \cdot 10^{-2}$	$9,64 \cdot 10^{-2}$	1569	147,96
3,85	4,81	$1,02 \cdot 10^{-1}$	$1,05 \cdot 10^{-1}$	$1,09 \cdot 10^{-1}$	1394	146,37
4,31	5,38	$1,11 \cdot 10^{-1}$	$1,17 \cdot 10^{-1}$	$1,21 \cdot 10^{-1}$	1243,5	145,49
4,76	5,94	$1,28 \cdot 10^{-1}$	$1,34 \cdot 10^{-1}$	$1,38 \cdot 10^{-1}$	1128	151,15
5,21	6,50	$1,41 \cdot 10^{-1}$	$1,49 \cdot 10^{-1}$	$1,54 \cdot 10^{-1}$	1035,5	154,29
5,66	7,05	$1,47 \cdot 10^{-1}$	$1,54 \cdot 10^{-1}$	$1,60 \cdot 10^{-1}$	958	147,53
6,54	8,13	$1,60 \cdot 10^{-1}$	$1,66 \cdot 10^{-1}$	$1,72 \cdot 10^{-1}$	836	137,78
7,41	9,19	$1,71 \cdot 10^{-1}$	$1,83 \cdot 10^{-1}$	$1,89 \cdot 10^{-1}$	744	136,15

*Commas represent decimal points.

Specific weights are shown in Table 2 and Fig. 1.

TABLE 2. SPECIFIC WEIGHTS OF THE SYSTEM $(CH_3)_4NI - I_2$ AT TEMPERATURES OF 130, 140 AND 150°

$\%(CH_3)_4NI$	d_{20}^{130}	d_{20}^{140}	d_{20}^{150}
0	3,9190	3,9049	3,9011
1,0	3,8766	3,8679	3,8009
3,0	3,7936	3,8023	3,8109
5,0	3,7218	3,7420	3,7608

*Commas represent decimal points.

fully stirred to accelerate dissolution of the iodide, it was again placed in the thermostat and kept there at 150° for 0.5-1 hour, after which electroconductivity was measured. Then the thermostat was cooled to 140°; after maintaining it at this temperature, measurements were made again. Later, following the same pattern, electroconductivity was measured at 130°. Then electroconductivity was repeatedly determined at 130, 140 and 150°, and even at higher temperatures.

Measurements made in this way were very similar for each temperature. The data given in Table 1 are averages.

To find the molecular electroconductivity with various concentrations $(CH_3)NI$, the specific weight of tetramethylammonium-iodide solutions in the melted iodine was determined. Specific weight was determined on a pycnometer with a calibrated neck. The pycnometer, containing a certain suspension of iodine or iodine alloyed with $(CH_3)_4NI$, was placed in a thermostat — a large glass beaker (with a stirring rod).filled with Vaseline oil — and kept for 30-40 minutes at 130°, then at 140 /755 and 150°. Later, in the same pycnometer, we determined the weight of corresponding volumes of water at 20° and thus calculated specific weights of d_{20}^{130}, d_{20}^{140}, d_{20}^{150}. The coefficient of expansion of the glass was not taken into consideration.

Molecular electroconductivity was calculated on the basis of $(CH_3)_4NI$ as the electrolyte.

Specific and molecular electroconductivity at 140° is given in Table 1 and /756 Fig. 2 and 3.

For comparison, Fig. 2 also shows the specific electroconductivity of iodine solutions of potassium iodide, according to the data of Lewis and Wheeler [2], and the electroconductivity of RbI, according to the data of Plotnikov, Fialkov and Chalyy [1].

Fig. 3 also shows the curves of molecular electroconductivity for iodides of alkali metals, taken from the works of the above named authors [1]. Although in this work the specific weights were calculated from the sum of volumes of melted iodine and solid salt, in this case, however, it could not lead to significant errors because, as shown by the comparison of specific weights of the system
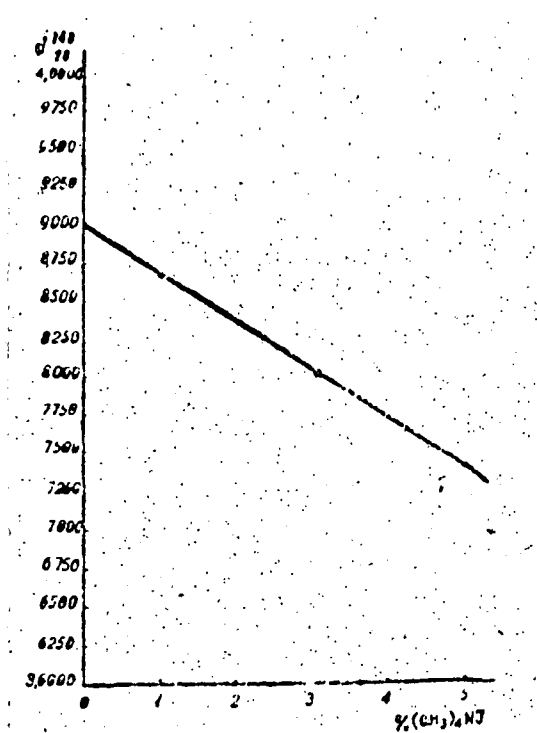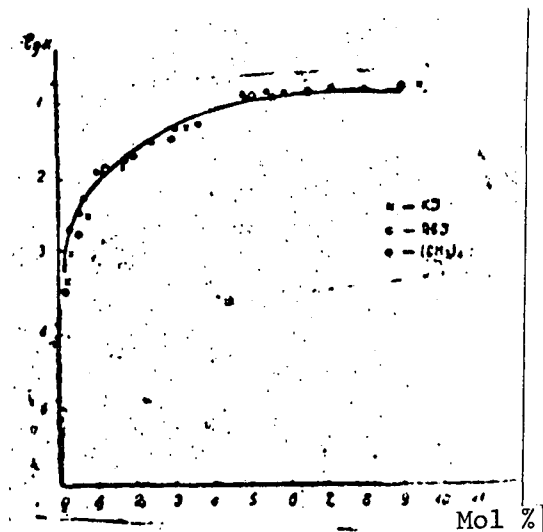
Figure 1

Figure 2

$(CH_3)_4NI-I_2$, determined experimentally and calculated from the sum of volumes of $(CH_3)_4NI$ and iodine, the specific weights practically coincide.

The specific electroconductivity of the system $(CH_3)_4NI-I_2$ increases rapidly with concentration, and even at 5 mol. % of $(CH_3)_4NI$ exceeds 10^{-1} mho. Subsequently, the increase in specific electroconductivity slows down and at 9.19 mol. % of $(CH_3)_4NI$ reaches only $1.7 \cdot 10^{-1}$ mho.

A comparison of the electroconductivity of the system $(CH_3)_4NI-I_2$ and iodine solutions KI or RbI shows that at low concentrations of iodides the electroconductivity of the system $(CH_3)_4NI-I_2$ slightly exceeds that of a system with KI or RbI. Thus, for example, X140° at 0.25 mol. % of $(CH_3)_4NI = 2.8 \cdot 10^{-3}$, at 0.5 mol. % it is $5.69 \cdot 10^{-3}$. At the same time, X140° for 0.28 mol. % of solution, KI = $1.19 \cdot 10^{-3}$, and for 0.51 mol. % of solution, RbI = $2.76 \cdot 10^{-3}$. With increased concentration, electroconductivities are leveled.

The electroconductivity isotherms of these three systems are the same.

An analogous conclusion can also be reached in relation to the molecular $\underline{/757}$ electroconductivity of these systems: isotherms of electroconductivity reach a maximum in the area of low iodide concentrations; the maximum of electroconductivity
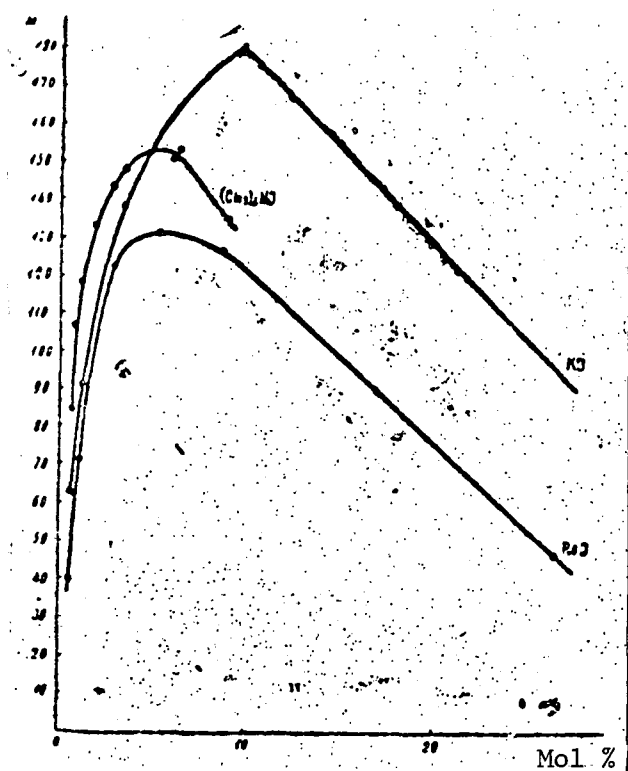
Figure 3

shifts somewhat (toward high concentrations) in the sequence of RbI, $(CH_3)_4NI$ and KI. In the same sequence, molecular electroconductivity also changes at the points of maximums.

The temperature coefficient of specific electroconductivity of the system $(CH_3)_4NI-I_2$ (see Table 3) changes in the same way as in the case of iodine solutions of KI and RbI: with low concentrations of $(CH_3)_4NI$, up to 0.2%, the temperature coefficient has a negative, gradually decreasing value. At 0.3-0.5%, the temperature coefficient is zero, and with subsequent increase of concentration becomes positive*; the positive value first increases, and then remains almost unchanged.

It must be noted that in the system $(CH_3)_4NI-I_2$, the change in the sign of the temperature coefficient occurs at much lower concentrations than in systems with KI (at 2.75%) and with RbI (at concentrations over 1.03%).

NATURE OF THE ELECTROLYTE

In solving this problem it is first of all necessary to take the fact into consideration that polyiodides are formed in the interaction of iodine $(CH_3)_4NI$. This was shown by the thermal analysis conducted by Olivari [11] and the preliminary works** of Geuther [13] and Stromholm [14].
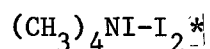
According to the diagram of fusibility, in the system $(CH_3)_4NI-I_2$, several iodides can be formed, beginning from the highest — enneaiodide $(CH_3)_4NI_9$ with a

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*This indicates that in iodide iodine solutions with low iodide concentrations a negative temperature coefficient appears, characteristic of melted iodine. With increased concentration of iodides, they begin to affect the changes in electroconductivity with temperature.

**$(CH_3)_4NI \cdot 4I_2$ obtained from alcohol solutions.

melting point of 106.4, according to the data of Olivari; 108° according to the data of Stromholm; 110° according to the data of Geuther. We measured the electroconductivity in the area of concentration (up to 9% mol) which corresponds to the formation of enneapolyiodide.

TABLE 3. TEMPERATURE COEFFICIENT OF ELECTROCONDUCTIVITY OF THE SYSTEM $(CH_3)_4NI-I_2$ *

Conc. wt. %	$C_1 \cdot 10^2$	$C_2 \cdot 10^2$	Note
0,10	—0,30	—0,22	Temperature coefficient was calculated according to the formula:
0,20	—0,05	—0,02	
0,30	0	0	$$C_i = \frac{(\lambda_2 - \lambda_1)\ 100}{\lambda_i(t_2 - t_1)}$$
0,50	+0,06	+0,04	
0,79	+0,12	+0,09	
0,99	+0,13	+0,13	C_1 — the temperature coefficient between X140° and X130°, relative to the average value of electroconductivity;
1,96	+0,33	+0,24	
2,43	+0,15	+0,22	
2,91	+0,38	+0,37	
3,38	+0,19	+0,21	
3,85	+0,30	+0,33	
4,31	+0,52	+0,43	C_2 — the temperature coefficient between 150 and 130°, relative to electroconductivity at 140°.
4,76	+0,46	+0,37	
5,21	+0,55	+0,44	
5,66	+0,47	+0,42	
6,54	+0,37	+0,36	
7,41	+0,73	+0,52	

*Commas represent decimal points.

It was necessary to find the resistance of this polyiodide at the measurement temperature (130-150°), to determine that it does not dissolve at that time with separation of iodine. For this purpose, polyiodide $(CH_3)_4NI_9$ was produced by the following method, which is not described in the literature. To an aqueous solution (approximately 0.5%) of $(CH_3)_4NI$, placed in a flask, was added an excess amount of the iodine solution in benzene [calculated with the formation of $(CH_3)_4NI_9$] and agitated. This causes rapid absorption of the iodine by the aqueous solution $(CH_3)_4NI$; the color of the benzene solution markedly lightens; large, heavy dark-colored drops collect on the bottom of the flask which are rapidly crystallized. The liquid was poured from the crystals, and they were filtered in a glass filter, washed with water and dessicated at 100°. A heavy fine-crystal power was obtained, dark greenish-brown in color, non-hygroscopic, stable in air. There was no dissolving with water during agitation: a separate aqueous liquid does not precipitate from the addition of a solution of $AgNO_3$. The melting point (in an open capillary) is 108°, the same as that which Stromholm indicates for producing his preparation.

Analysis of the crystals: the amount of iodine was determined according to Foldgard after reduction with a solution of sodium sulfite; the amount of nitrogen was determined according to the Kjeldahl method.

0.2236 g material: 0.2437 g I.
0.2772 g material: 0.2539 g I.
Found %: I 91,75; 91.61.

$(CH_3)_4NI_9$. Calculated %: I 93.90.
4.9668 g material: 0.0566 g N_2.
Found %: N 1.14.
$(CH_3)_4NI_9$. Calculated %: N 1.15

Thus, it can be considered proven that the system we studied contains a poly-iodide $(CH_3)_4NI_9$, which does not dissolve at the temperature of measuring electro-conductivity.

In solving the problem of the nature of the electrolyte in the system $(CH_3)_4NI-I_2$, the results of determining the molecular condition $(CH_3)_4NI$ in the iodine solution must be given much consideration.

According to cryoscopic measurements, conducted by Olivari [16], the molecular weight of $(CH_3)_4NI$ — in concentrations up to 3.79% mol. — changes from 216.1 (at 0.11%) to 261.5 (at 0.71%), then decreases to 171 (at 3.79%).

We decided to repeat cryoscopic measurements of the system $(CH_3)_4NI-I_2$, using a Beckmann instrument constructed in a way to prevent the evaporation of iodine vapors and the entrance of moisture.

In calculations of molecular weight, we used the cryoscopic constant for iodine, determined by Beckmann, which is 204 (based on 100 g of iodine)*.

We calculated the molecular weight by the ordinary formula $M = \dfrac{g \cdot 100k}{G \, \Delta t}$, in which g is the suspension of dissolved material, and G is the suspension of the solvent.

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*According to the data of Olivari, the cryoscopic constant for iodine is 213 [17].

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TABLE 4. CRYOSCOPY OF THE SYSTEM $(CH_3)_4NI-I_2$; $M_{(CH_3)_4NI}=201.06$; $M_{(CH_3)_4NI_9}=1216.34$

susp. of iodine g	Susp. of $(CH_3)_4NI$ g	wt. %	Δt	M_1	M_2
77,25	—	—	—	—	—
	0,0773	0,10	0,12	170,1	1035,0
	0,3865	0,43	0,47	217,1	1348,8
	0,7725	0,99	0,875	232,3	1486,7
	1,1588	1,48	1,35	326,6	1485,0
	1,5451	1,96	1,96	222,8	1402,0

We calculated the molecular weight, first of all, based on $(CH_3)_4NI$ as the dissolved material. The values obtained, shown in the table in the M_1 column, are similar to those obtained by Olivari [16], although somewhat lower (approximately 10-12%) in the area of the average concentrations we measured. As in Olivari's work, with increased concentration, molecular weight first increases and then begins to decrease.

This kind of change in molecular weight with concentration has already been noted in the literature in relation to several electrolyte systems. It affects the presence of complexing processes — a combination with the solvent or polymerization of the dissolved material — and the fact that the electrolytes in these systems are molecules of the material produced. With increased concentration of this material, the number of molecules dissociable in the iodine also increases, which leads to a reduction in the apparent value of molecular weight.

It must be pointed out that in cryoscopic measurements of iodine solutions of alkali metal iodides [3] and thallium iodide [4], a reduction was also observed in the apparent association factor with increased iodide concentration.

If we take into consideration the presence in this system of the polyiodide of tetramethylammonium $(CH_3)_4NI_9$ with a molecular weight of 1216.34 which does not dissolve at the measurement temperature, then the values of molecular weight are too low, although they exceed* the formula molecular weight for $(CH_3)_4NI$, being 210.06.

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*In concentration close to 0.3% $(HC_3)_4NI$.

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We, therefore, felt it was necessary to calculate the molecular weight from the results of cryscopic measurements, based on ennea polyiodide as the dissolved substance. For this, we added to the suspension of $(CH_3)_4NI$ an amount of iodine corresponding to the formation of $(CH_3)_4NI_9$, and the number obtained in this way was inserted in the formula to calculate molecular weight (instead of g). The amount of solvent was reduced correspondingly. These values are given in Table 4 in column M_2. The change in molecular weight with concentration is the same as for values calculated using $(CH_3)_4NI$ as the dissolved material.

Molecular weight of a polyiodide slightly exceeding the formula value (apparent association factor $M_2/M_{theor.}$ is 1.11-1.22), affects the formation in this system of associated molecules of the polyiodide with a common formula $[CH_3)_4NI_9I]_n$.

The low apparent association factor and at the same time the considerable electroconductivity of the system $(CH_3)_4NI-I_2$, indicating a high degree of electro-lytic dissociation, implies that the actual association factor of a polyiodide of tetramethylammonium-iodide is 2.

The general conclusion that can be made from an analysis of our results and a comparison with literature data is that the electrolyte in the system $(CH_3)_4NI-I_2$, in the concentration interval we studied, is associated molecules of ennea poly-iodide $[(CH_3)_4NI_9]_2$. It is very likely that this can explain the similarity of the isotherm of electroconductivity of the system $(CH_3)_4NI-I_2$ and the system iodine-iodides of alkali metals (as well as the system iodine-TlI), in which electrolytic dissociation is experienced by associated molecules of iodides.

CONCLUSIONS

1. The electroconductivity of the system iodine-tetramethylammonium-iodide, measured up to 9.2 mol. % of $(CH_3)_4NI$ at 130, 140 and 150°, increases rapidly with concentration, and at 5 mol. % already reaches 10^{-1} mho. The increase in specific electroconductivity later slows down, and at 9.19 mol. % $(CH_3)_4NI$ $X_{130°} = 1.71 \cdot 10^{-1}$, and $X_{150°} = 1.89 \cdot 10^{-1}$.

2. A comparison of specific and molecular electroconductivity of the system $(CH_3)_4NI-I_2$ and iodine solutions KI and RbI show a great similarity of the electro-conductivity isotherms of these systems in value and change with concentration

and temperature.

3. Results of thermal analysis of the system $(CH_3)_4NI-I_2$, (according to the data of Olivari) and cryoscopic measurements, as well as study of the properties of the enneapolyiodide of tetramethylammonium implies that the electrolyte in the system $(CH_3)_4NI-I_2$ in the concentrations studied is associated molecules of the polyiodide with the probable formula $[(CH_3)_4NI_9]_2$.

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